MAGNETIC SUSCEPTIBILITY AND LIGAND FIELD BEHAVIOUR OF PURE AND DILUTED CRYSTALS OF $FeSiF_6 \cdot 6H_2O$

MANJU MAJUMDAR AND SUNIL K. DATTA

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32.

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ABSTRACT. The magnetic anisotropy and susceptibility of $FeSiF_6 \cdot 6H_2O$ have been measured in the temperature range 300°-90°K. No phase transition has been observed in this crystal, in contrast to the case of the isomorphous cobalt and manganese salts. Measurements on crystals diluted with $ZnSiF_6.6H_2O$ in ratios of 1 : 1 and 1 : 10 show that the diluent ions do not radically modify the nature and symmetry of the ligand field at the ferrous ion, as in the latter cases. However, the experimental data may be fitted with a refined theory (which includes the effects of the trigonal field and the spin orbit interaction and the covalency factors) on the plausible assumption that the anisotropic field parameter changes with temperature, the variations being more drastic in the dilute crystals than in the pure in the temperature range studied. The available e.s.r. data have been analysed in the light of the above findings.

INTRODUCTION

Among the hexahydrated fluosilicates of the iron group of elements, the ferrous salt is one of the most extensively studied from the magnetic and optical (including e.s.r. and Mössbauer spectra), as well as structural standpoints. The neutron diffraction analysis of the crystal by Hamilton (1962) shows the space group to be $R\bar{3}m$ with one molecule in the unit cell. Each Fe^{2+} ion is surrounded by six oxygens from the ligands, the octahedron being *elongated* along the [111] axis which coincides with the trigonal axis of the crystal. On the other hand, the magnetic susceptibility data of Jackson (1959) and Ohtsuka (1959) in the range 77°-1°K show that the susceptibility along the trigonal axis, $\chi_{\parallel}$, is smaller than that in the normal direction, $\chi_{\perp}$, apparently indicating that the octahedron is *squat*, on the point charge model approach (see discussions).

The theory of the magnetic susceptibility of the crystal was worked out by Palumbo (1958) to explain Jackson's data, using the Spin Hamiltonian technique. However, only the lowest three levels in the ligand field and spin-orbit perturbations were taken into account on the assumption that $\Delta >> |\lambda|$, where Δ is the trigonal field splitting parameter and λ the spin-orbit coupling coefficient.

In calculating the electric quadrupole moment of 14.4 keV state of ^{57}Fe from the Mössbauer spectra of $FeSiF_6$, $6H_2O$, Eicher (1963) (see also Johnson, *et al.*, 1962; Ono and Ito, 1964) deduced expressions for fine structure energy

levels and magnetic susceptibility. He showed that the value of Δ which had been taken to be 1200 cm^{-1}, was too high and should be $\sim$ 750 cm^{-1} to fit the susceptibility as well as the electric quadrupole moment data. However, he did not consider the effects of the overlap of the 3d electron orbitals with the ligand oxygen orbitals. These effects have been taken into account by Bose and Rai (1965).

Previous investigations on other isomorphous crystals of this series, e.g., the manganese (Tsujikawa and Couture, 1955), cobalt (Majumdar and Datta, 1965) and copper salts (Thesis, Majumdar 1966, unpublished) reveal a phase transition in the region 220°—270°K with the formation of a 'hybrid' crystal (Ubbelohde and Woodward, 1945) of a lower symmetry at low temperatures. Our magnetic data on the cobalt and copper salts indicate a drastic change in the ligand field symmetry and strength which accompanies the phase transition in these crystals. On diluting the crystals with the zinc or manganese salts the occurrence of the phase transition was found to be dependent on the nature of the diluent. It may be noted here that the neutron diffraction data (Hamilton, 1962) do not show any evidence of an order-disorder transformation in $FeSiF_6.6H_2O$ down to 90°K.

In the present work we have investigated the magnetic behaviour of the undiluted ferrous salt, as well as those diluted with the zinc salt in different proportions with a view to studying phase transition effects if any, and to correlate the refined theory of Bose and Rai (1965) with our experimental data in the range 300°—90°K, as also those of Jackson (1959) at 77°K and lower.

EXPERIMENT AND RESULTS

Ferrous fluosilicate was prepared by dissolving 99.9% pure iron wire in cold dilute hydrofluosilicic acid (prepared by the gradual action of powdered quartz with dilute hydrofluoric acid). The solution was concentrated in a desiccator connected to a water pump and crystallized over sulphuric acid in a nitrogen atmosphere. The pale green prismatic crystals gave an assay value of 99.5% Fe^{2+} and were almost indefinitely stable when stored in a cool and dry atmosphere. The zinc salt was prepared from reagent quality zinc carbonate and H_2SiF_6, followed by evaporation and crystallization. Mixed crystals were prepared and analysed in the usual manner. In all cases repeated fractional crystallization was performed to achieve the highest degree of purity.

The magnetic anisotropy, $\Delta\chi$, of the crystals was measured in a torsion balance reported earlier (Majumdar and Datta, 1965). No detectable anisotropy was observed down to 90°K in the plane normal to the trigonal (c) axis in either the pure or the diluted crystals. Measurements in different planes containing the c axis gave identical anisotropy, as shown in figure 1, which includes results for two such orientations. Neither any sharp change in colour nor any abnormal thermal expansion of the crystal was observed. These facts reveal that these ferrous

salts do not undergo any change in crystallographic, and hence magnetic symmetry in the temperature range studied, in contrast to the case of the cobalt and cobalt-manganese mixed crystals.

For the measurement of magnetic susceptibility, χ_i, a Curie-type torsional balance designed by Bose *et al.*, (1964) was used. The crystal was mounted with the *c*-axis vertical and the susceptibility measured in the horizontal plane. The

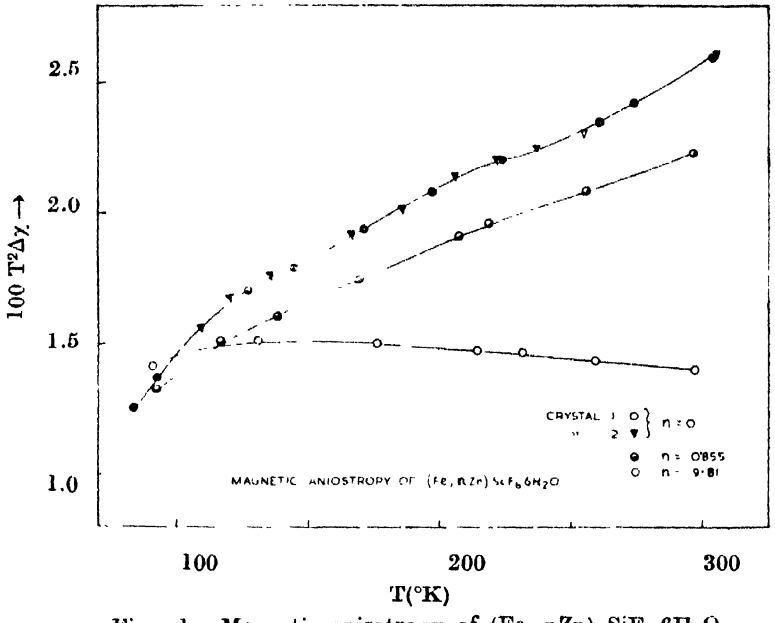

Fig. 1. Magnetic anisotropy of (Fe, nZn) $SiF_6.6H_2O$.

observed values of anisotropy and susceptibility, $(\Delta\chi)_{obs}$ and $(\chi_i)_{obs}$, per gm. mole of the mixed crystal were corrected for the diamagnetism of the constituents from the relationship :

$$(\chi_\perp - \chi_\parallel)_p = (\chi_\perp - \chi_\parallel)_{obs} - (n+1)(\chi_\perp - \chi_\parallel)_{Zn} \quad (1)$$

$$(\chi_i)_p = (\chi_i)_{obs} - (n+1)\chi_{i_{Zn}}$$

where the quantities with the suffix p stand for the $Fe(H_2O)_6^{2+}$ complex, the subscript Zn denotes the zinc salt and in (2) the suffix i stands for $\parallel$ and $\perp$, n being the number of moles of the zinc salt per mole of the ferrous salt (evidently n is zero for the undiluted crystal when the residual diamagnetic term in (1) refers to the Fe^{2+} salt only), the *difference* in the diamagnetism of the ion cores of Fe^{2+} and Zn^{2+} being neglected in comparison with $\Delta\chi$ and χ_i. The diamagnetic susceptibilities of the zinc salt were found to be : $\chi_\perp = -135.8$ and $\chi_\parallel = -136.6$ in the usual 10^{-6} cgs em units, and were found to be temperature independent.

The anisotropy data for $n = 0$, 0.855 and 9.81 are shown in figure 1. However, the susceptibility data for only the first two are shown in figure 2, since the

relatively large dilution in the remaining crystal rendered the susceptibility values somewhat inaccurate. The *interpolated values* of the anisotropy and susceptibilities at 20°C intervals of temperature for the pure and the I : 0.855 crystals are presented in tables I and II, respectively.

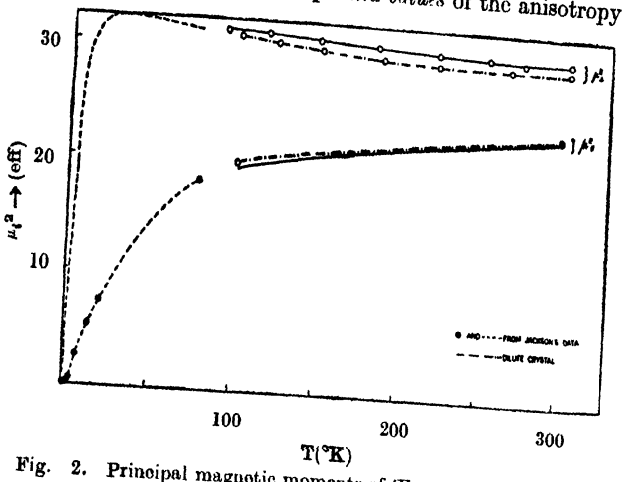

Fig. 2. Principal magnetic moments of (Fe, nZn) $SiF_6.6H_2O$.

THEORY OF TRIGONALLY DISTORTED $Fe(H_2O)_6^{2+}$ COMPLEX

The ground state $3d^6\ {}^5D$ of Fe^{2+} ion is split in a field of O_h symmetry into a ground triplet, ${}^5T_2$, and an upper doublet, ${}^5E$. Optical spectra of the pure crystal as also that containing 10% of the Fe^{2+} salt (Agnetta *et al.*, 1962) show a main vibronic band at 10.58 kK (1 kK = 10^3 cm^{-1}) which remains practically unchanged in position at 300°, 90° and 4°K, so that the difference between the mean cubic field levels may be taken to have this value. The wave functions for the ${}^5T_2$ state may be written as (labelling a state with its M_L value) :

$$T_{2g}^{+} = \sqrt{\frac{2}{3}}\ |2> - \sqrt{\frac{1}{3}}\ |-1>$$

$$T_{2g} = |0> \qquad \ldots (3)$$

$$T_{2g}^{-} = \sqrt{\frac{2}{3}}\ |-2> + \sqrt{\frac{1}{3}}\ |1>$$

while those for the upper ${}^5E$ state are

$$E_g^{+} = \sqrt{\frac{1}{3}}\ |2> + \sqrt{\frac{2}{3}}\ |-1>$$

$$E_g^{-} = \sqrt{\frac{1}{3}}\ |-2> - \sqrt{\frac{2}{3}}\ |1> \qquad (4)$$

Under a trigonal distortion of the octahedral field the split components of $T_{2g}\pm$ will mix with those of $E_g\pm$ from which it is possible to calculate the admixtural coefficients $\alpha_{\|}$, $\alpha_{\perp}$ along and normal to the trigonal field axis (Abragam and Pryce, 1951; Bose and Rai, 1965). In our present work we shall take $\alpha_{\|}$, $\alpha_{\perp}$ to be adjustable parameters. We then make use of the fact that the set of wave functions (3) behave as atomic P-functions with an effective orbital quantum number $L' = 1$. Using the technique of Abragam and Pryce (1951) we classify the states according to the $m(= M_{L'}+M_S)$ values. The Hamiltonian for the trigonal field and spin-orbit interaction is then written as

$$H = \Delta(1-L'_z{}^2)+\zeta_{\|}L'_zS_z+\zeta_{\perp}(L'_xS_x+L'_yS_y) \qquad \ldots (5)$$

where $\zeta_i (i = \| \text{ or } \perp)$ is the spin orbit coupling coefficient along and normal to the trigonal axis, reduced from the free ion value and rendered anisotropic because of covalent overlap between central ion and ligand charge clouds.

The 15×15 matrix corresponding to $M_{L'} = 1, 0, -1$ and $M_S = 2, 1, 0, -1, -2$ can then be broken up into two cubic (for $m = 0$, $m = \pm1$, the former further reducing to a quadratic and a linear equation), a quadratic (for $m = \pm2$) and a linear (for $m = \pm3$) equations. The final expressions for the nine energy values are :

(a) $m = 0$:

$$\left.\begin{aligned} E_s &= \tfrac{1}{2}[(\alpha_{\|}\zeta_{\|}+\Delta) \pm \{(\alpha_{\|}\zeta_{\|}-\Delta)^2+24\alpha_{\perp}\zeta_{\perp}{}^2\}^{\frac{1}{2}}] \\ &\qquad (-ve \quad \text{for} \quad s = 0, \quad +ve \quad \text{for} \quad s = 5) \\ E_s &= \alpha_{\|}\zeta_{\|} \quad (\text{for } s = 4) \end{aligned}\right\} \qquad \ldots (6)$$

(b) $m = \pm1$:

$E_j = \alpha_{\|}\zeta_{\|}x_j$ $(j = 1, 3, 6)$ where x_j's are the roots of the cubic equation

$$x^3-(2+A)^2x^2+(2A-5B^2)x+6B^2 = 0 \qquad \ldots (7)$$

$$A = (\Delta/\alpha_{\|}\zeta_{\|}), \quad B = (\alpha_{\perp}\zeta_{\perp}/\alpha_{\|}\zeta_{\|})$$

(c) $m = \pm2$:

$$E_t = \tfrac{1}{2}[(\Delta-\alpha_{\|}\zeta_{\|})\pm\{(\Delta+\alpha_{\|}\zeta_{\|})+8\alpha_{\perp}\zeta^3{}_{\perp}\}^{\frac{1}{2}}]$$

$$-ve \quad \text{for } t = 2, \quad +ve \text{ for } t = 7 \qquad \ldots (8)$$

(d) $m = \pm3$:

$$E_8 = -2\alpha_{\|}\zeta_{\|}. \qquad \ldots (9)$$

Here, and in the following expressions the suffix j stands for $p = 1, 3, 6$, s for $p = 0, 4, 5$, and t for $p = 2, 7$, $p = 0, 1, \ldots 8$ representing the nine energy levels. The levels corresponding to E_s are singlets, while the rest are doublets.

The principal magnetic susceptibilities of the $Fe(H_2O)_6^{2+}$ complex, $K_{\|}$ and $K_{\perp}$ along and normal to the trigonal axis, are then calculated from the first and second order Zeeman terms,

$$<\psi_{nm}|\mu|\psi_{nm}> \text{ and } \sum_{n,m} \frac{|<\psi_{nm}|\mu|\psi_{n'm'}>|^2}{E_n - E'_{n'}}$$

where the magnetic moment operator μ takes the form

$$\mu_{\|} = \beta(-\alpha_{\|} k_{\|} L_z' + 2S_z)$$

and

$$\mu_{\perp} = \beta\left[-\tfrac{1}{2}\alpha_{\perp} k_{\perp}(L_+' + L_-') + (S_+ + S_-)\right]$$

for the $\|$ and $\perp$ directions of the ligand field, respectively. The final expression for susceptibility is

$$K_\eta = \frac{N\beta^2}{kTZ}\left[\frac{1}{T}\left\{\sum_{p=0}^{8} G_{1\xi}^{(p)} \exp\left(-\frac{E_p - E_0}{kT}\right)\right\}\right.$$

$$\left. + 2k\left\{\sum_{p=0}^{8} G_{2\xi}^{(p)} \exp\left(-\frac{E_p - E_0}{kT}\right)\right\}\right] \qquad \ldots \quad (10)$$

where $\xi = z$ for $\eta = \|$

and $\xi = x = y$ for $\eta = \perp$,

$G_{1\xi}^{(p)}$ and $G_{2\xi}^{(p)}$ are the first and the second order Zeeman terms defined above, Z is the partition sum $\sum_p W \exp(E_0 - E_p)/kT$, W being the degeneracy of the p-th level. In the following expressions for the G's, q is a floating index which takes the values as indicated.

$$G_{1z}^{(j)} = 2\{\alpha_{\|} k_{\|}(c_j^2 - a_j^2) + 2b_j^2 + 4c_j^2\}^2 \quad j = 1, 3, 6$$

$$G_{1z}^{(s)} = 0$$

$$G_{1z}^{(t)} = 2[b_2^2(2 - \alpha_{\|} k_{\|}) + 4a_2^2]^2 \quad \text{for} \quad t = 2$$

and

$$= 2[a_2^2(2 - \alpha_{\|} k_{\|}) + 4b_2^2]^2 \quad \text{for} \quad t = 7$$

$$G_{1z}^{(8)} = 2(4 - \alpha_{\|} k_{\|})^2$$

$$G_{2z}^{(j)} = \sum_q \{2(4 + \alpha_{\|} k_{\|}) c_j c_q + 2b_j b_q - \alpha_{\|} k_{\|} a_j a_q\}/(E_q - E_j)$$

$$(q = 1, 3, 6; \quad q \neq j)$$

$$G_{2z}^{(t)} = 2(2 + \alpha_{\|} k_{\|})^2 a_2 b_2/(E_q - E_j) \quad (q = 2, 7; \quad q \neq t)$$

$$G_{2z}^{(s)} = \Sigma \{2 | <s | \mu_{||} | q> |^2/(E_q - E_s)$$

$$q(= 0, 4, 5; \quad q \neq s)$$

$$| <s | \mu_{||} | q> |^2 = 2a_0^2(2+\alpha_{||}k_{||})^2 \quad \text{for } s, q = 0, 4$$

$$= 2b_0^2(2+\alpha_{||}k_{||})^2 \quad \text{for } s, q = 4, 5$$

$$= 0 \quad \text{for } s, q = 5, 0$$

$$G_{2x}^{(s)} = 0$$

$$G_{1x}^{(p)} = 0$$

$$G_{2x}^{(j)} = \sum_s 2A_{sj}^2/(E_s - E_j) + \sum_t 2B_{tj}^2/(E_t - E_j)$$

$$G_{2x}^{(s)} = \sum 2A_{sj}^2/(E_j - E_s)$$

$$G_{2x}^{(t)} = \sum_j 2B_{tj}^2/(E_j - E_t) + 2C_t^2/(E_t - E_8)$$

$$G_{2x}^{(8)} = \sum_t 2C_t^2/(E_t - E_8).$$

where

$$A_{sj} = \sqrt{6}\,(a_0a_j + b_0b_j) - \frac{\alpha_\perp k_\perp}{\sqrt{2}}\,(a_jb_0 + b_ja_0) + 2c_ja_0, \; (s = 0)$$

$$A_{sj} = \sqrt{3}a_j + \frac{b_jk_\perp}{\sqrt{2}} - \sqrt{2}c_j, \; (s = 4)$$

$$A_{sj} = \sqrt{3}(b_0a_j - 2a_0b_j) - \frac{\alpha_\perp k_\perp}{\sqrt{2}}\,(b_0b_j - 2a_0a_j,)$$

$$+ \sqrt{2}b_ob_j \; (s = 5)$$

$$B_{tj} = (\sqrt{6}\,b_2a_j + 2a_2b_j) - \frac{\alpha_\perp k_\perp}{\sqrt{2}}\,(b_2b_j + a_2c_j), \; (t = 2)$$

$$B_{tj} = (\sqrt{6}a_2a_j - 2b_2b_j) - \frac{\alpha_\perp k_\perp}{\sqrt{2}}\,(b_ja_2 - c_jb_2), \; (t = 7)$$

$$C_t = \left(2b_2 - \frac{\alpha_\perp k_\perp}{\sqrt{2}}\,a_2\right), \; (t = 2)$$

$$= \left(2a_2 + \frac{\alpha_\perp k_\perp}{\sqrt{2}}\,b_2\right), \; (t = 7)$$

$$a_0 = \{\sqrt{3}\ \alpha_\perp\ \zeta_\perp /(\alpha_\parallel \zeta_\parallel - E_0)\} b_0;\quad 2a_0^2 + b_0^2 = 1$$

$$a_j = \frac{\sqrt{3}(2\alpha_\parallel \zeta_\parallel - E_j)}{\sqrt{2E_j}}\ c_j\ ;\quad b_j = \frac{2\alpha_\parallel \zeta_\parallel - E_j}{\sqrt{2}\alpha_\perp\ \zeta_\perp}\ c_j$$

$$a_j + b_j^2 + c_j^2 = 1$$

$$a_2 = \frac{\sqrt{2}\ \alpha_\perp\ \zeta_\perp}{\Delta - E_2} b_2;\quad a_2^2 + b_2^2 = 1$$

and k_i's ($i = \parallel, \perp$) are the orbital reduction factors along and normal to the three-fold axis of the complex.

DISCUSSIONS

Our magnetic measurements show the absence of any phase change in ferrous fluosilicate, as has been observed in the manganese, cobalt and copper salts. The structure of all these salts appears to be the same at room temperature (Pauling, 1930) and is a close-packed one. The reason why phase transition occurs in only some of these crystals and not in others is not yet clear. The thermal stability of the crystals is probably more directly related to the geometry of the packing and lattice dynamical conditions than to the configurational instability of the metal-ligand complex arising from the electronic degeneracy of the central ion (Jahn Teller effect). It may be noted that both Co^{2+} and Fe^{2+} have an orbital triplet level lying lowest in a cubic field which splits leaving lowest either a singlet or a Kramers' doublet under the action of the lower symmetry field and spin orbit coupling and should, therefore, be stabilized against Jahn-Teller distortions (Van Vleck, 1960).

Because of the non-occurrence of a phase transition in either of the Fe^{2+} and Zn^{2+} salts in the temperature range studied, the effect of the latter in the mixed crystals is mainly to 'dilute' former ions in the lattice, in contrast to the case of the Co, Zn mixed crystals whose magnetic (and similar) properties are quite different from those of the cobalt salt which shows a phase transition at low temperatures (Majumdar and Datta, 1965). Thus, for instance, the $T^2 . \Delta\chi$ vs. T curve for the Fe^{2+} salt and that diluted with about an equal part of Zn^{2+} are very similar (see figure 1). However, the slope of these curves decreases with increasing dilution, indicating that the strength of the anisotropic ligand field and its thermal variation is dependent upon changes in the crystal lattice brought about by dilution and their induced effects on the primary $Fe(H_2O)_6^{2+}$ cluster (Van Vleck, 1939). The effect of dilution on the e.s.r. g-values is discussed later.

In calculating the energy levels from the above theory one observes that the lowest level turns out to be a singlet for negative values of Δ while it is a doublet for positive values of it. The susceptibility data of Jackson (1959)

at low temperatures, as well as our data at high temperatures can be explained only on the assumption of negative values of Δ. The resulting energy level structure and the nature of the thermal variation of susceptibility are mainly responsible for the observed fact that $\chi_\perp > \chi_\parallel$ in the temperature range studied, although the $Fe(H_2O)_6$ octahedron is shown to be elongated from the neutron diffraction data (Hamilton 1962).

In correlating the theoretical expressions for the susceptibilities of the ionic complex, K_i, with the experimental values, χ_i, ($\chi_i \equiv K_i$, there being one molecule in the unit cell), we have obtained by trial and error a set of values of α_i, k_i, ζ_i ($i = \parallel, \perp$) and Δ which would give the best fit with the anisotropy and susceptibility data. We have assumed the first three parameters to be temperature independent, only Δ being assumed to vary with temperature (Bose, *et al.* 1960, *et seq.*). As mentioned earlier, Eicher (1963) chose the variable to be the Figgis parameter δ ($= \Delta/|\lambda|$). He found that δ varied with temperature in the range 1°—77°K from 6 to 9 in the perpendicular direction but remained constant at 7.5 in the axial direction. However, there seems to be absolutely no reason why δ should be different in the two directions and vary with T in only one of them while remaining constant in the other. Furthermore, as already mentioned, he did not take into consideration the covalency factors, as we have done here. In the table III we have given the values of the fixed parameters at the top and have shown how Δ has to be varied with T to give a good fit with the experimental data.

The values of the parameters $\alpha_i k_i$ and $\alpha_i \zeta_i$ chosen here are of the expected order of magnitude, since the admixture coefficients α_i are likely to be only slightly less than 1, the spin orbit coupling being small; furthermore, the orbital and spin orbit reduction factors are generally known to be between 0.8 and 0.9 for the $M(H_2O)_6^{2+}$ complexes. The energy levels thus calculated have been labelled here as E_0, E_1, ... E_8 in order of increasing energies. It may be noted that the calculated values of the moments, μ_i, are much less sensitive to variations in $\alpha_i k_i$ and $\alpha_i \zeta_i$ than to changes in Δ in the temperature range studied. For the sake of completeness we have included the experimental data of Jackson (1959)* in the range 4.2° and 77°K in the above table and have also shown the calculated values obtained with the chosen ligand field parameters. It will then be seen that Δ has to be varied from -685 cm^{-1} at 300°K to -830 cm^{-1} at 77°K and then changed to -730 cm^{-1} at 4.2°K for the undiluted crystal. For the diluted crystal, however, the variations are much larger, Δ changing from -600 cm^{-1} at 300°K to -1065 cm^{-1} at 100°K. The substitution of Zn^{2+} for Fe^{2+} in the dilute crystal thus appreciably affects the ligand field behaviour of the $Fe(H_2O)_6^{2+}$ complex.

*The values of $\chi_\perp$ had to be obtained by suitable transposition of his graph for $\chi_\perp \cdot T$ vs. T, and are necessarily approximate.

TABLE I

Magnetic anisotropy and susceptibilities of $FeSiF_6.6H_2O$ (interpolated values in 10^{-6} cgs e.m. units)

T(°K)	$\Delta\chi$	$\chi_\perp$	$\chi_\parallel$	$\bar{\chi}$
300	2,854	12,467	9,613	11,516
280	3,121	13,325	10,204	12,285
260	3,457	14,350	10,893	13,198
240	3,906	15,587	11,681	14,285
220	4,534	17,091	12,557	15,580
200	5,230	18,900	13,670	17,157
180	6,117	21,167	15,050	19,128
160	7,313	23,938	16,625	21,501
140	9,036	27,436	18,400	24,424
120	11,424	32,183	20,759	28,375
100	14,570	38,800	24,230	32,944
90	16,457	43,122	26,665	37,633

TABLE II

Magnetic anisotropy and susceptibilities of $FeSiF_6.6H_2O$, $n ZnSiF_6.6H_2O$ (interpolated values, in 10^{-6} cgs e.m. units), (n = 0.855).

T(°K)	$\Delta\chi$	$\chi_\perp$	$\chi_\parallel$	$\bar{\chi}$
300	2,484	12,144	9,660	11,316
280	2,760	13,030	10,260	12,109
260	3,108	14,023	10,915	12,987
240	3,522	15,252	11,730	14,078
220	4,060	16,680	12,620	15,327
200	4,683	18,421	13,738	16,859
180	5,518	20,593	15,075	18,754
160	6,650	23,300	16,650	21,083
140	8,245	26,835	18,590	24,087
120	10,522	31,628	21,100	28,113
100	13,850	38,625	24,775	34,008

TABLE III

Thermal variation of the anisotropic field parameter, Δ, in

(a) $FeSiF_6.6H_2O$:

$\alpha_{\parallel}k_{\parallel} = 0.8$; $\alpha_{\perp}k_{\perp} = 0.8$; $\alpha_{\parallel}\zeta_{\parallel} = -87\ cm^{-1}$; $\alpha_{\perp}\zeta_{\perp} = -90\ cm^{-1}$

T(°K)	$-\Delta$ cm^{-1}	$\mu_{\parallel}$		$\mu_{\perp}$	
		obs.	calc.	obs.	calc.
300	685	4.802	4.812	5.463	5.460
250	730	4.752	4.732	5.468	5.465
200	770	4.676	4.650	5.497	5.487
150	800	4.573	4.550	5.534	5.500
100	815	4.401	4.365	5.570	5.540
	(from Jackson's data, 1959)				
77.3	830	4.247	4.227	5.50	5.53
20.4	780	2.715	2.752	5.75	5.826
4.2	730	0.758	0.782	4.44	4.51

(b) $FeSiF_6.6H_2O$, $nZnSiF_6.6H_2O$: (n = 0.855)

$\alpha_{\parallel}k_{\parallel} = 0.8$; $\alpha_{\perp}k_{\perp} = 0.8$; $\alpha_{\parallel}\zeta_{\parallel} = 92\ cm^{-1}$; $\alpha_{\perp}\zeta_{\perp} = 94\ cm^{-1}$

300	600	4.817	4.835	5.495	5.510
250	900	4.743	4.758	5.459	5.484
200	930	4.690	4.650	5.422	5.425
150	950	4.561	4.550	5.399	5.400
100	1065	4.497	4.470	5.403	5.412

Since the lowest level in ferrous fluosilicate is nondegenerate, E_0, and the next higher level, E_1, lies over 10 cm^{-1} higher up, no e.s.r. spectra can be observed in this crystal with the microwave frequencies and magnetic fields ordinarily used (Abragam and Pryce, 1951). E_1 being a doublet will of course, be split by the magnetic field, and an e.s.r. signal, if observed, will correspond to a forbidden transition. Some estimates of the effective g-values were therefore made by Palumbo (1958) from the susceptibility of Jackson (1959). Using a third order perturbation technique and considering only the three lowest energy levels, he showed that good fit with the experimental data could be obtained at low temperatures on the assumption $\Delta >> |\lambda|$, if one used a fictituous spin quantum number, $S' = 2$ in the usual Spin Hamiltonian formula. The following values were deduced : $g_{\parallel} = 2.00$; $g_{\perp} = 2.12$; $D = 10.9\ cm^{-1}$; $\Delta = 1200\ cm^{-1}$. Almost the

same values were arrived at by Ohtsuka (1959) from his own a.c. susceptibility data at low temperatures. The fit with the experimental data above 77°K is very poor, apparently because of increased population of E_3 and higher levels at high temperatures.

Rubins (1962) has reported e.s.r. data in Fe, Zn mixed fluosilicates. He deduced the $g_{\parallel}$-values somewhat indirectly in crystals containing 2, 10, 20 per cent of the Fe^{2+} salt as 2.38, 2.4, 2.2, while $g_{\perp}$ in only the first crystal was estimated as 2.6. These have been ascribed to transitions between the $M_s' = \pm 1$ doublet. For the undiluted crystal $g_{\parallel}$ was found to be ~ 9, ascribed by him to transitions in the $M_s' = \pm 2$ doublet. These transitions, usually forbidden, were assumed to occur because of second order splitting of the Zeeman levels.

We have calculated the first order g-values for transitions within the E_1 doublet from the corresponding wave functions $\psi\pm$ using the relationship :

$$g_{\parallel} = 2|\langle\psi_1|-\alpha_{\parallel}k_{\parallel}L_z'+2S_z|\psi_1\rangle|\,; \quad g_{\perp} = 2|\langle\psi_1|-\alpha_{\perp}k_{\perp}L_x'+2S_x|\psi_{-1}\rangle|$$

which come out as : $g_{\parallel} = 3.88$, $g_{\perp} = 0$, which are considerably different from those reported by Rubins. This apparently arises from the extensive substitution of Zn^{2+} for Fe^{2+} in the crystal lattice which modifies the ligand field behaviour at the Fe^{2+} ion in the crystal.

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